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Effect of the Evaporation Temperature of a Tetraphenyl-Tetramethyl-Trisiloxane (Dow-Corning 704) Precursor on the Properties of Silicon Containing Diamond-Like Carbon (Si-DLC) Coatings Synthesized by Ion-Beam-Assisted Deposition (IBAD)

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ARL-TR-1942 May 1999

Abstract

Hard, adherent, and low-friction amorphous Si containing diamond-like carbon (Si-DLC) coatings has been synthesized both by 40-keV and 2.5-keV Ar ion-beam-assisted deposition (IBAD) of a tetraphenyl-tetramethyl-trisiloxane $(C_6H_5)_4(CH_3)_4Si_3O_2$ oil onto Si wafer substrates. The sp^3 and sp^2 bonding ratio of the coatings was investigated with the aid of Fourier-transform infrared (FTIR) microspectroscopy and valence band x-ray photoelectron spectroscopy (XPS). In addition, the effect of the oil evaporation rate on film morphology is also discussed.

Acknowledgments

This work was sponsored by the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground (APG), MD. The authors would like to acknowledge the assistance of Mr. Keith Bendyk with data formatting.

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1. Introduction

Films of many promising tribological materials, including conventional diamond-like carbon (DLC), have been successfully deposited by ion-beam-assisted deposition (IBAD). The friction coefficient of unlubricated DLC films in dry gases can be as low as 0.01, but this value can reach as high as 0.10 and 0.20 when measured in a 10% relative humidity [1–3]. However, it has been shown by various researchers [2–4] that DLC films containing elements such as Si and Ti retain low pin-on-disk friction coefficients in humid environments. DLC films containing Si (Si-DLC) exhibit friction coefficients as low as 0.04 [2–4] at ambient humidity and temperature and are therefore highly promising for tribological applications. Several trial industrial applications of DLC have been reported, including protective-wear coatings on bearings and forming tools [5], but these applications are limited because of the poor thermal stability of DLC above 350° C.

In this report, we report on the atomic bonding and the morphology of IBAD Si-DLC coatings synthesized with both 40-keV and 2.5-keV Ar ion beams.

2. Experimental

A ZYMET 100 nonmass-analyzed ion implanter was used for the synthesis of one batch of Si-DLC coatings using energetic 40-keV Ar ion bombardment (10 μAcm^2) of a vapor-deposited tetraphenyl-tetramethyl-trisiloxane (Dow-Corning 704) diffusion pump oil. The diffusion pump oil precursor was evaporated from a heated Cu oil container through a 3-mm-diameter, 2-mm-thick aperture. The oil evaporation temperature was varied from 125° C to 155° C in steps of 5° C. The Si substrates were initially cleaned in methanol and acetone and then sputter-cleaned with a 40-keV Ar ion beam (4.5 μAcm^2) for 10 min. The temperature of the substrate was maintained close to room temperature using heat-conducting vacuum grease to hold the sample on a water-cooled stage. The substrate was inclined at 45° with respect to both the horizontal ion beam and the vertical flow direction of the vaporized oil. The aperture to substrate distance was 0.15 m with a shutter placed above the oil container to start and stop the oil deposition. The growing film surface was

continuously bombarded by an Ar ion beam at 40 keV. The base pressure was 2.66×10^{-4} Pa (3×10^{-5} torr) pressure as in previous work [4]. All coating deposition runs lasted 190 min. In a second experiment, IBAD was performed using an effuser (Epion Inc.) providing constant beam vapor intensity across the substrate and two saddle field ion guns (Ion Tech, UK) operating at 2.5 keV. In this case, the same organic precursor was used and the temperature set at 140° C. This system produced a combined ion beam that was less collimated and produced a range of current densities from 0.2 to 1.2 μAcm^2.

The thickness of the films produced at 40 keV was measured with the aid of a profilometer. A ball-on-disk tribometer with a 1.27-cm-diameter (1/2 in) 440C alloy steel ball under 0.5 N load was used to determine the unlubricated sliding friction coefficient μ.

The coatings were investigated with the aid of optical microscopy, synchrotron infrared (IR) microspectroscopy, performed at the National Synchrotron Light Source at Brookhaven National Laboratory (2.5-keV-processed coatings only) and valence band x-ray photoelectron spectroscopy (XPS) performed on a VG ESCA CLAM II system to correlate the sp^3/sp^2 bonding ratio to processing parameters and morphology.

3. Results and Discussion

3.1 Si-DLC Formed by 40-keV IBAD Processing.

3.1.1 Composition and Coating Morphology. The composition of the Si-DLC coatings, according to our previous work [4, 6], remained constant. It has been shown that the relative ratios of C, Si, and O in the IBAD coatings were found to be approximately the same as the precursor: C:Si:O = 14:1.5:1. This strongly suggests that the siloxane backbone (Si-O-Si-O-Si) of the precursor molecule remains intact during the ion irradiation process, and only C:H and C:C bonds are broken to convert the oil to hard DLC.

The surface of the coatings gradually became visually less stained and more reflective with increasing oil evaporation temperature.

3.1.2 Growth Rate, Microstructure, and Adhesion. The average growth rate, thickness, and ball-on-disk of the synthesized Si-DLC coatings produced are shown in Table 1. Since the ion energy was kept constant, the growth rate difference of these coatings is attributed to the higher number of oil molecules, per minute and per area, reaching the substrate surface. No delamination was observed while testing the adhesion of the coatings to their underlying Si substrates either by the so-called scotch-tape test or indirectly during ball-on-disk wear-test measurements.

Table 1. Summary of Measured Properties of Si-DLC Coatings Deposited on Si as a Function of the Oil Evaporation Temperature

Temperature (°C)	Thickness (nm)	Growth Rate (nm/min)	Friction Coefficient (μ average)
125	370	1.95	0.10
130	520	2.75	0.10
135	759	3.95	0.10
140	1,180	6.20	0.10
145	1,580	8.30	0.10
150	1,800	9.50	0.10
155	2,550	13.40	0.10

3.1.3 Sliding Friction Coefficient and Wear Rate. The average, unlubricated, ball-on-disk sliding friction coefficient of all these coatings was 0.10 after 300-m traveled distance, in agreement with our previous results [4, 6]. The beginning of graphitization of the Si-DLC coating was indicated on the obtained friction vs. distance (Figure 1) shown by the abrupt (downward) change of the slope of the curves during the initial 50-m traveled distance. Meletis and coworkers [7, 8] have attributed the smaller friction coefficient of their conventional DLC and our Si-DLC coatings to their graphitization due to frictional heating generated by the rotating steel ball on the coating surface during the ball-on-disk testing. The wear rate of all coatings, determined with the aid of a stylus profilemeter, was of the order of 10^{-13} m^3.

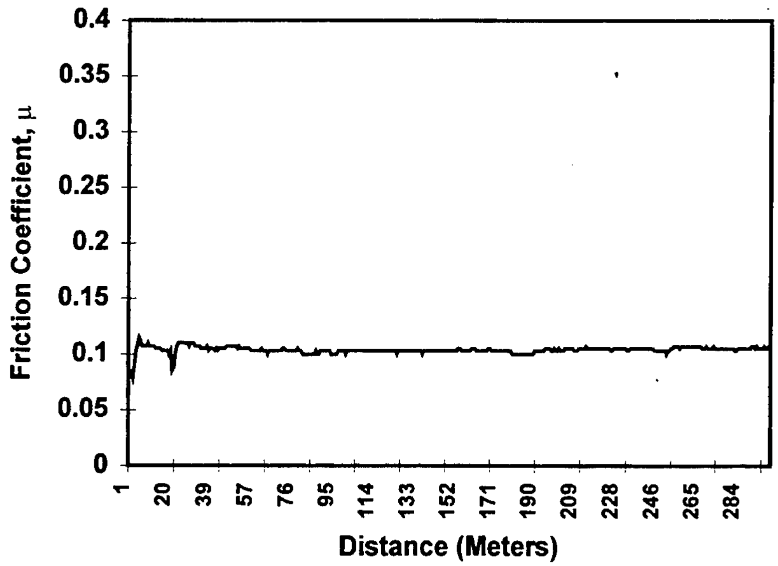

Figure 1. Unlubricated Ball-on-Disk Friction Coefficient of Si-DLC Coatings Synthesized With a 40-keV, 10-μAcm^2 Ar Ion Beam and Oil Evaporation Temperature at 145° C.

3.1.4 Morphology of the Si-DLC Coatings. In Figure 2, we show how the morphology of the coatings varied with temperature of effusion from 125° C (10^{-3} torr) to 155° C (10^{-2} torr). It can be seen that the low-temperature effusion resulted in heterogeneities best described as hillocks, which gradually give way to greater coating uniformity as the temperature of effusion is increased. In Figure 2, we have also shown the corresponding valence band XPS spectra. While it is apparent that the spectra are difficult to resolve comprehensively, we can comment on four carbon-bonding features indicated in the figure. In agreement with the valence band analysis of Serin et al. [9], it is apparent in Figure 2 that C2pπ (sp^2 band) is most clearly evident between 125 and 130° C. This band is merged into the $2p_\sigma$ sp^3 band at 135° C, which, in turn, becomes a more dominant component of the two at and above 140° C. This would suggest that both sp^2- and sp^3-hybridized bonds are formed in all of the previously mentioned Si-DLC coatings, but that greater diamond-like character is observed at the higher precursor vapor pressures, which is also consistent with more uniform morphology.

3.2 Si-DLC Formed by 2.5-keV IBAD Processing: Composition and Coating Morphology. The Ar ion current density distributions were mapped for the dual-saddle field gun system (Figure 3). Associated with variations of ion current density across the substrate surface were corresponding

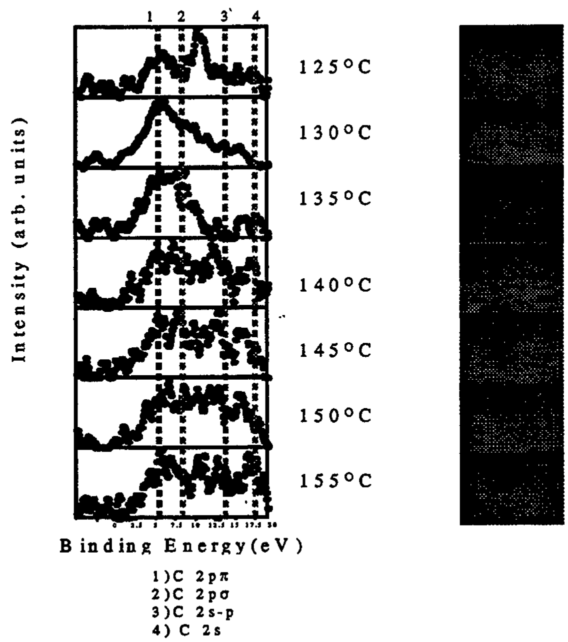

Figure 2. Valence Band XPS and Photomicrographs (200× Magnification) of Si-DLC Coatings.

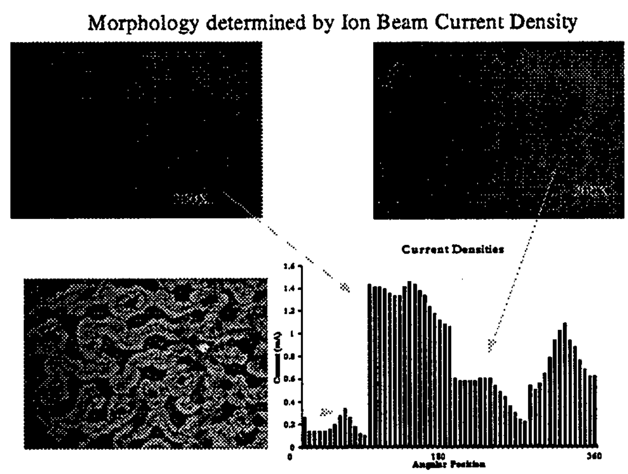

Figure 3. Argon Ion Current Densities and Photomicrographs (200× Magnification) of Si-DLC Formed by 2.5-keV IBAD Processing.

changes in film morphology. As seen from Figure 3, current densities of ~0.2 μAcm^2 resulted in morphologies typical of dewetting of polymeric films. Current densities of the order of 0.5 μAcm^2 were associated with more homogeneous films exhibiting small hillocks similar to the 40-keV,

10-μAcm^2 films described previously. By contrast, featureless planar films were generated by ion current densities of the order of 1.4 μAcm^2.

We examined the lowest and highest current density films with synchrotron IR microspectroscopy. As shown in Figure 4, the greatest absorbance was observed for the highest current density, which clearly showed sp^2 and sp^3 bonding character, as well as Si-O-Si antisymmeteric stretching. The latter corroborates the earlier observation from compositional analysis for the 40-keV films. It is seen from Figure 4 that the low-current density-processed film exhibited strong absorbance corresponding to out-of-plane bending of CH_3, which dominates the spectrum over the signal from the vibrational state of Si-O-Si and is indicative of a more polymeric type of film.

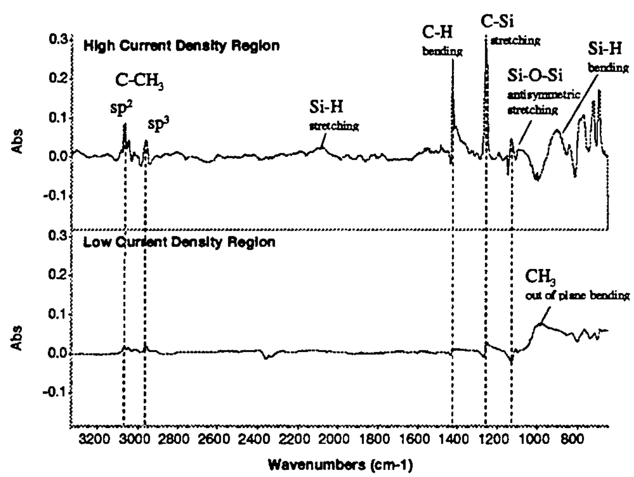

Figure 4. Synchrotron FTIR Spectra From Si-DLC Formed by 2.5-keV IBAD Processing.

4. Conclusions

The morphology and molecular structure of Si-DLC formed by IBAD has been shown to be strongly dependent on the relative arrival rates of the organic precursor vapor and the bombarding Ar ions.

We have shown from preliminary spectroscopic studies that the complex nanocomposite structure resulting from IBAD can be elucidated by a combination of valence band XPS and IR microspectroscopy.

More detailed analysis of these films combining SIMS and Auger spectroscopy is needed to improve the current model of molecular structure of Si-DLC coatings.

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 1999	Interim, Jan 97–Aug 98

4. TITLE AND SUBTITLE
Effect of the Evaporation Temperature of a Tetraphenyl-Tetramethyl-Trisiloxane (Dow-Corning 704) Precursor on the Properties of Silicon Containing Diamond-Like Carbon (Si-DLC) Coatings Synthesized by Ion-Beam-Assisted *

5. FUNDING NUMBERS
LIFX02

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: AMSRL-WM-MC
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8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-1942

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

10.SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
* Deposition (IBAD)
**State University of New York at Stony Brook, Stony Brook, NY 11794-2275

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS	15. NUMBER OF PAGES
evaporation temperature, precursor, properties, coatings, IBAD	15
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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